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Unoccupied surface electronic structure of Gd(0001)

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The unoccupied surface electronic structure of Gd(0001) was investigated with high-resolution inverse-photoemission spectroscopy. An empty surface state near E_F is observed at $\bar{\Gamma}$. Two other surface-sensitive features are also revealed at 1.2 and 3.1 eV above the Fermi level. Hydrogen adsorption on Gd surfaces was used to distinguish the surface-sensitive features from the bulk features. The unoccupied bulk-band critical points are determined to be Γ_3^+ at 1.9 eV and A_1 at 0.8 eV.

I. INTRODUCTION

The surface electronic structure of the rare earth metals has attracted considerable attention recently. The interest has not only been stimulated by the general curiosity regarding these relatively less studied systems, but also by the close connection between the electronic structure and the unusual surface magnetic properties.¹⁻⁵ A new surface state near E_F has been observed on Gd(0001) surfaces of the ordered Gd overlayers on W(110) with photoemission.^{6,7} This was later confirmed on Tb(0001) and Gd(0001) single crystal surfaces^{8,9} and proved to be spin polarized.^{10,11} The existence of such a state is in agreement with the recent theoretical calculations¹² and is connected with the altered coupling at the surface,¹³ and therefore the enhanced surface magnetic ordering of Gd and Tb.^{1,2}

The technical improvements in obtaining well-ordered clean surfaces of rare earth metals has made the studies of surface electronic structure easier to undertake. The Gd films grown on a W(110) substrate provides a system where the preparation of the surface is easier to approach compared with the bulk, while ordering similar to that of the bulk is obtained.^{2,14,15}

While the Gd epitaxial films and single crystals have been studied by photoemission,^{6-11,16,17} only a few inverse-photoemission studies have been performed with limited results on the unoccupied surface electronic structure of Gd.¹⁸ The theoretical calculation predicted the opposite spin component of the surface state near E_F in photoemission above E_F with an exchange splitting of 0.9–1.0 eV at ground state.¹² In this work, we investigate

the surface electronic structure of Gd(0001) grown on a W(110) substrate with inverse photoemission. Since hydrogen adsorption forms a well-defined layer of hydrogen only at the surface region,¹³ it has been used as a way to test the surface sensitivity of the features. A surface state feature is observed near E_F , along with two other surface-sensitive features.

II. EXPERIMENT

The experiment was carried out on a high-resolution inverse-photoemission spectrometer with photon energy range of 8–30 eV. The energy resolution varies from 0.26 eV half-width at full maximum at 11.5 eV to larger at higher energies (0.6 eV at 20.5 eV). The accuracy of the energy calibration is 0.1 eV. The pressure of the spectrometer chamber was in the 10^{-11} torr range. All the energies of the unoccupied states are referenced to the Fermi level.

Gd(0001) surfaces were prepared by evaporating gadolinium onto the W(110) single crystal substrate at room temperature.^{6,15} The W(110) single crystal was cleaned with the normal procedure (oxygen treatment followed by flashing) (Ref. 19) in the attached preparation chamber. Gadolinium was evaporated from an electron-beam heating evaporator at the rate of 1–3 Å/min in the preparation chamber. The pressure during evaporation was kept at $1-2 \times 10^{-10}$ torr or lower in order to ensure the purity of the films. The films were then annealed to 530 K to remove defects yet without resulting in island formation.¹⁵ Hydrogen dosing was undertaken

in the 10^{-8} torr range with a UHV leak valve and was measured in units of Langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ torr sec}$). Both the hydrogen adsorption and inverse-photoemission measurements were undertaken at room temperature.

III. RESULTS

Figure 1 shows the inverse-photoemission spectra of two Gd films. Compared with the spectra of clean W(110),²⁰ tungsten features are not detected with the gadolinium film thicknesses employed for this work. At normal incidence, a feature shows up near E_F (0.25 eV with the current resolution), which persists even for the films as thin as 3 Å. We assign this feature as an unoccupied surface state based on its surface sensitivity, presence in a gap of the projected bulk band, and lack of k_{\perp} dependence. As shown in Fig. 1, the intensity of this feature is strongly reduced by hydrogen adsorption. For Gd(0001) hydrogen adsorption is known to occur mainly at the Gd surface region and affects the surface electronic structure.¹³ Oxygen adsorption or exposure to the ambient gas at 10^{-11} torr for several hours can also decrease the intensity of this feature substantially. Off-normal measurements (not shown in the figures) show that the intensity of this feature does not change significantly with changing k_{\parallel} until halfway across the Brillouin zone, where it disappears indicating the dispersion toward the occupied side of the Fermi level. Such a state cannot be attributed to the Gd bulk bands. In almost all the bulk-band calculations, there is no Gd 5d state around E_F until 0.4–0.7 eV above E_F along the $\Gamma\Delta A$ direction (Γ , perpendicular to our sample surface).^{21–23} In other words, there is a gap between the occupied Γ_4^- and the unoccupied A_1 in the projected band along the $\Gamma\Delta A$ direction. The feature we observed is therefore not a Gd bulk band but instead a surface state.

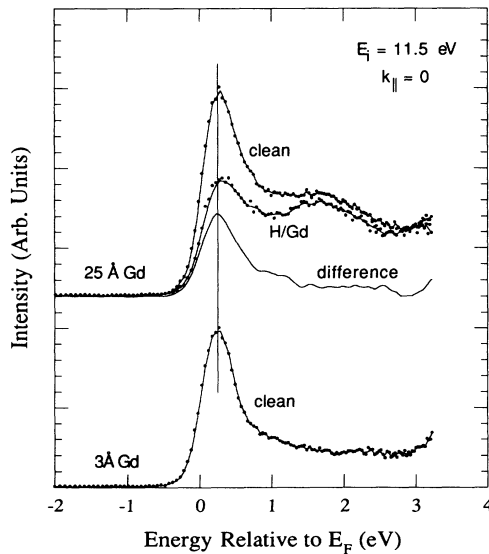


FIG. 1. Inverse photoemission spectra taken at normal emission with electron incidence energy of 11.5 eV. The effect of hydrogen adsorption on the 25-Å film is shown by the spectrum on the hydrogen-covered surface and its difference with that of the clean surface.

The assignment of the surface state is further supported by Fig. 2. At normal emission, the sharp feature near E_F shows no shift other than the apparent resolution changes with different incident electron kinetic energies, i.e., no dispersion with k_{\perp} . This demonstrates the two dimensionality of this state.

In contrast, the broad feature at around 1.8 eV in Fig. 1 is neither altered by hydrogen adsorption (no feature around 1.8 eV in the difference spectrum in Fig. 1) nor as sensitive to contamination as the surface state. This feature is apparent only when the film is thick enough (more than several monolayers thick) and is an unoccupied 5d bulk band of gadolinium. It is seen from Fig. 2 that this feature displays energy dispersion with k_{\perp} as expected for the bulk bands, especially at low incident electron energies. For the hcp lattice [0001] direction (C_{6v}), the dipole selection rule allows the transitions $\Delta_1 \rightarrow \Delta_1$, $\Delta_2 \rightarrow \Delta_2$ (p -polarized light) and $\Delta_1 \rightarrow \Delta_6$, $\Delta_2 \rightarrow \Delta_5$ (s -polarized light).²⁴ Without light polarization detection, all the unoccupied bulk bands in our energy range (up to several eV above E_F) are dipole allowed. The hcp bands can be unfolded into the band structure similar to that of the fcc [111] direction with Δ_1 , Δ_6 (Λ_1 , Λ_3 in the fcc label) at one side and Δ_2 , Δ_5 (also Λ_1 , Λ_3 in the fcc label) at the other.^{16,24} Since any transition between the bands at two different sides is dipole-forbidden, such an unfolded band structure is more physical and is easy to compare with experiments involving dipole transitions. Compared to bulk-band calculations,^{21–23} the band assignments are given as indicated in the figure.

From the extrema of the band dispersion, we can determine two critical points of the Gd unoccupied bulk

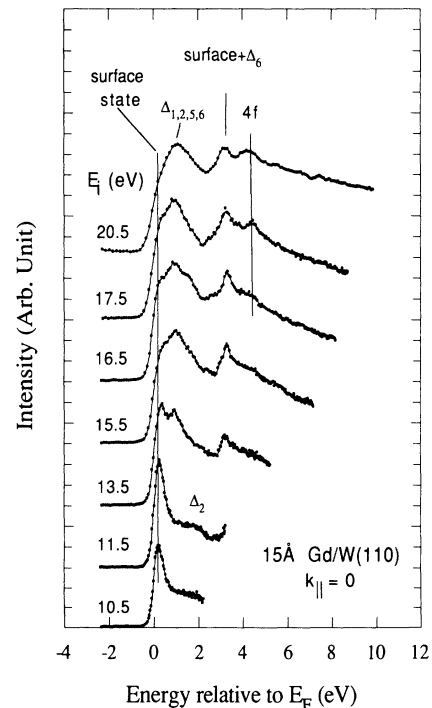


FIG. 2. Energy dependence of the inverse-photoemission features of the Gd(0001). The intensities are normalized to the incident currents.

band structure at 1.9 ± 0.1 eV (Γ_3^+) and 0.8 ± 0.1 eV (A_1), which suggests an inner potential of about 13.4 eV. No band mapping, however, was performed mainly due to the difficulty on accurately determining the inner potential with a limited energy range and the relatively large k broadening caused by the short electron mean free path in Gd (1–3 Å in our energy range). Our measurements were done at room temperature, which is slightly higher than the bulk Curie temperature (293 K), yet lower than the surface Curie temperature (> 310 K).^{2,4,5} The bulk-band critical points given in this work are therefore for the paramagnetic phase.

The feature at 4.1 eV in Fig. 2 corresponds to the unoccupied Gd 4f states. It becomes more prominent towards higher electron energies because of the energy dependence of the 4f cross section, and does not exhibit dispersion being a localized core level. Compared to the bulk 4f peak position measured at much higher electron kinetic energies,²⁵ we observe a clear downwards shift of 0.3–0.4 eV. This is attributed to a surface core-level shift. By fitting two lines with the experimental bulk line shape to our data, we obtain a surface core level shift of –0.4 eV, i.e., to lower energy, which is the same as for the occupied 4f state. More surprisingly, this empty 4f level shifts to higher energy upon oxygen exposure, i.e., opposite to the shift of the occupied 4f under the same conditions. With 3–4 L of oxygen, the empty 4f is shifted by +1.0 eV, while the occupied one is shifted by –1.0 eV. Detailed data analysis and further discussion in terms of initial state vs final state effects of the 4f core level shifts is provided elsewhere.²⁶

The surface electronic structure can be revealed with the assistance of hydrogen adsorption even when those states are overshadowed by bulk bands, as demonstrated in Fig. 3. For a thick film of 25 Å, several features overlap with each other and are hard to recognize. After adsorbing hydrogen onto the Gd surface, the spectrum changes dramatically and several sharp features can now be discerned in the difference spectra. From photoemission studies, it is clear that the adsorbed hydrogen atoms tend to remain at the surface and mainly affect the electronic structure of the surface.¹³ The features in the difference spectra are therefore the states that are more surface sensitive. While we have identified the surface-sensitive feature near E_F as a surface state, there are two other surface-sensitive features at 1.2 and 3.1 eV at an incidence energy of 13.5 eV (Fig. 3). The trace of the 1.2 eV feature can also be seen in Fig. 1 for an incidence energy of 11.5 eV, and exists at different thicknesses. This feature could be a surface resonance or a bulk band which is more sensitive to hydrogen adsorption than the rest of the bulk-band structure. With hydrogen adsorption, it is clear that the 3.1 eV surface feature is located on top of a very broad bulk feature, which is the rapidly dispersing unoccupied Δ_6 band. Both the surface and bulk features contribute to the feature at 3.1–3.2 eV in Fig. 2, which has only a very small dispersion with electron energy, i.e., k_{\perp} . The feature at 3.1 eV above E_F displays a small energy dispersion away from normal incidence, suggesting an effective mass of about $4m_e$.

No hydrogen-induced surface state and/or surface res-

onance was observed in our experiments. The hydrogen-induced features should have a negative intensity, or a dip, in the difference spectra. The dip at 0.8 eV in the spectra shown in Fig. 3, however, always appears at the energy position of the bulk band for the films of different thicknesses. On the other hand, the dip in the spectra of different electron energies appears at different energy positions. This dip, therefore, is not caused by any hydrogen-induced surface state or surface resonance shifted in energy from the one on the clean surface.

We observed that the electrons used for inverse-photoemission measurements also result in electron-stimulated hydrogen desorption. Our spectra of H/Gd were taken by repeatedly saturating the Gd surface through hydrogen exposure between several short periods (500 s) of data acquisition, which were later added up for better statistics. As shown in Fig. 3, gradual recovery of the features for the clean surfaces occurs by keeping the sample under the electron gun at the energies where our inverse-photoemission experiments were performed. The spectra can therefore change with measuring time and appear to further resemble that of the clean surfaces with time. The difference spectra of the H/Gd and after electron-stimulated desorption show similar features

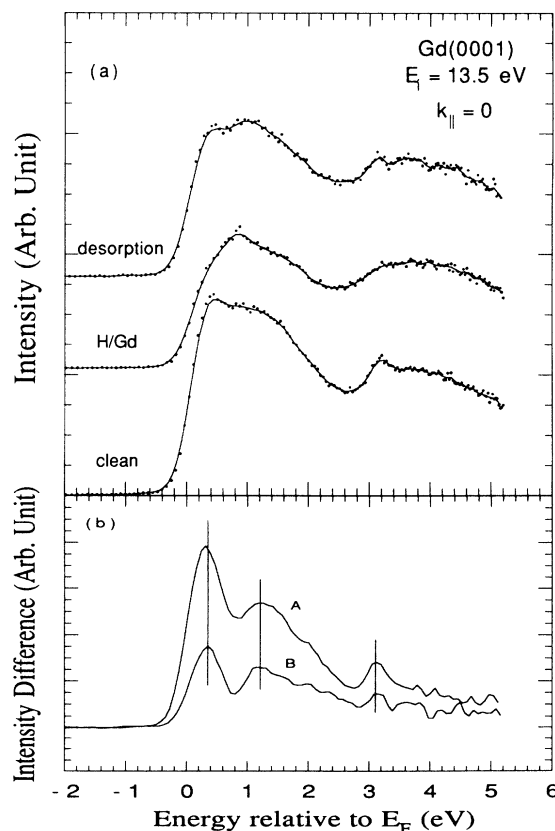


FIG. 3. Effect of hydrogen adsorption and electron-stimulated desorption. (a) Spectra of the clean surface, hydrogen-covered surface, and H/Gd after exposure to the electron beam for about 30 min. (b) Intensity differences between spectra of the clean and hydrogen-covered Gd surface, A, and between the spectrum after electron-stimulated desorption and the spectrum of hydrogen-covered surface, B.

as the difference between the clean and hydrogen-covered surfaces, which again suggests the surface sensitivity of those features.

The experimental surface states and/or surface resonances and bulk-band critical points of Gd along $\Gamma\Delta A$ are summarized in Fig. 4, along with a nonrelativistic paramagnetic bulk-band calculation.²² Besides the unoccupied states from this work, the occupied bands at room temperature from previous work are also included for completeness. Notice that the gap between Γ_4^+ and A_1 leaves a projected gap around E_F , in which lie the surface states near E_F .

IV. DISCUSSION

The surface state near E_F observed in inverse photoemission is close in energy to the surface state ($E_b = -0.1$ – 0.2 eV) observed in photoemission.^{6,7} Both the occupied and unoccupied surface states near E_F follow the same dispersion trend (little dispersion near the zone center and dispersing downward halfway cross the Brillouin zone). Compared with the bulk bands, the surface state in photoemission has larger intensity. It is likely that both of them are split off from the same Gd $5d$ state. Since our experiments were performed at room temperature, the one observed in inverse photoemission could be either the tail of the one observed in photoemission, which is broad at finite temperature, or its opposite spin part. While the surface state in photoemission is spin polarized, the spin polarization of the state in inverse photoemission has yet to be confirmed. In addition, we cannot completely rule out the possibility of having yet another surface state right above E_F at $\bar{\Gamma}$ with a different symmetry character.

Similar surface states near E_F have been observed for Tb(0001),⁸ Ti(0001),²⁷ and La(0001) (Ref. 28) with photoemission, and Y(0001) (Ref. 29) and La(0001) (Ref. 28) with inverse photoemission. It is most likely, therefore, that the existence of such a d_{z^2} surface state near E_F is a common feature near the zone center for these hcp metals with similar lattice constants. It should be noted, however, that the occupied surface state of Gd exhibits strong spin polarization at low temperature,^{10,11} which is not expected for nonmagnetic metals like Y, La, and other nonmagnetic rare-earth metals. It is not surprising that this d -like surface state becomes spin polarized in ferromagnetic Gd and plays an important role on surface magnetism,^{13,12} while an equivalent role of this state does not exist for nonmagnetic hcp metals.

The state at 1.2 eV is likely to be a surface resonance which is the opposite spin part of the surface state near E_F as predicted by the surface band calculation.¹² Confirmation of this assignment, however, awaits spin-polarized measurements. Another possibility is that this state at 1.2 eV is a bulk band which is more surface sensitive than the other bulk bands. If it is indeed the counterpart of the surface state near E_F , our measurements indicate an exchange splitting of 1.2 ± 0.2 eV for the surface state, which is larger than that of the bulk band (0.6–0.8 eV).^{21,23,9} It is consistent with an enhanced magnetic coupling and therefore enhanced Curie temperature at the Gd(0001) surface. Such an exchange split-

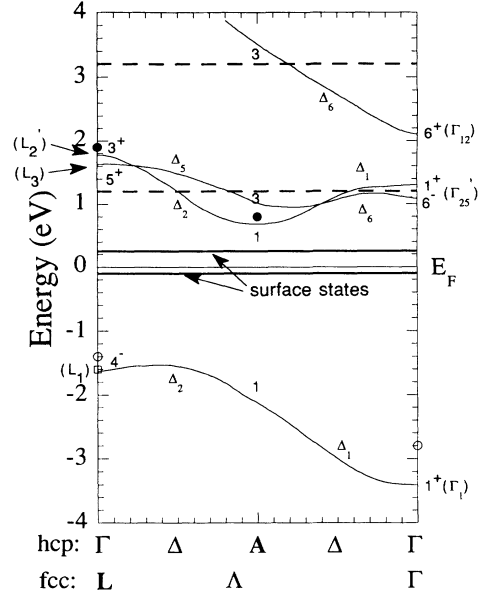


FIG. 4. Experimental surface states and/or surface resonances (thick lines) and bulk-band critical points (solid circles from this work, open circles from Ref. 16, and open square from Ref. 9), in comparison with a paramagnetic bulk-band structure along $\Gamma\Delta A$ (thin lines) for gadolinium (energies in eV with respect to the Fermi level). The gap around E_F is apparent in the bulk-band structure calculation. The bands are unfolded according to Ref. 24 similar to the d bands of fcc metals. Besides the hcp labels, some fcc labels are given in brackets for comparison.

ting of the surface state is also consistent with the band calculations.¹²

The third surface-sensitive feature at 3.1 eV could be either an image state or another surface resonance of Gd pulled out from the upper Δ_6 band. An image state is normally located several tenths of an eV below the vacuum level of the surface and has a large free-electron-like energy dispersion away from normal incidence. The feature at 3.1 eV is just 0.2 eV below the vacuum level of the clean Gd(0001) surface.^{16,13} The heavy effective mass of about $4m_e$ and the relatively small binding energy of such an image state is probably caused by imperfection of the surface. On the other hand, at $\bar{\Gamma}$, in addition to the surface state and/or surface resonance near E_F and about 1 eV above E_F , the slab band calculations of Gd(0001) also predicted states at around 3 eV and 2 eV above E_F with more than 50% weight in the surface muffin-tin sphere for both ferromagnetic and antiferromagnetic configurations of the surface spins in respect to that of the bulk.¹² The calculated band at around 3 eV is clearly derived from the Δ_6 bulk band and is in agreement with our observations. We cannot confirm the presence of any surface sensitive feature around 2 eV.

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